REPORT DOCUMENTATION PAGE

Public Reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comment regarding this burden estimates or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188,) Washington, DC 20503.

1. AGENCY USE ONLY (Leave Blank)	2. REPORT DATE February 21, 2000	3. REPORT TYPE AND DATES COVERED Technical Report

4. TITLE AND SUBTITLE
Demonstration of a Split-Operator Numerical Method for Modeling Sorption and Degradation Processes

5. FUNDING NUMBERS
DAAG55-98-1-0221

6. AUTHOR(S)
Joseph A. Pedit and Cass T. Miller

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
CB 7400, 104 Rosenau Hall
University of North Carolina
Chapel Hill, NC 27599-7400

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

U. S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSORING / MONITORING AGENCY REPORT NUMBER

ARO 37661.6-EV

11. SUPPLEMENTARY NOTES
The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.

12 a. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release; distribution unlimited.

12 b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

Mathematical models for simulating contaminant fate and transport often include mass transfer, nonlinear reactions, multiple species, and multiple dimensions. These problems can require significant computational effort. Split operator numerical methods can be used to significantly reduce the computational demands of simulating some of these problems. We demonstrate a split operator numerical method on a model for sorption and degradation processes.

20000707 115

14. SUBJECT TERMS split operator, numerical method, sorption, degradation	**15. NUMBER OF PAGES** 15
	16. PRICE CODE

17. SECURITY CLASSIFICATION OR REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION ON THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL

Technical Report

Technology Transfer of Basic Research on Multiphase Subsurface Fate and Transport

Contract/Grant Number: DAAG55-98-1-0221

Demonstration of a Split-Operator Numerical Method
for Modeling Sorption and Degradation Processes

Joseph A. Pedit and Cass T. Miller

Center for the Advanced Study of the Environment

The University of North Carolina at Chapel Hill

February 21, 2000

Introduction

The purpose of this report is to demonstrate the use of a split-operator (SO) numerical method on a problem of interest to Waterways Experimental Station (WES). Many of the environmental problems of interest to WES include advective and dispersive transport and reaction processes. Mathematical models for simulating environmental processes that include mass transfer, nonlinear reactions, multiple species, and multiple dimensions can require significant computational effort. SO methods can be used to significantly reduce the computational demands of simulating some of these problems. We demonstrate a SO numerical method on a model for sorption and degradation processes. Data provided by WES was used for the simulations.

Modeling Methods

In this section we describe the mathematical models used to interpret the batch and column data provided by WES (*Natural Attenuation of Explosives in Soil and Water Systems at DoD Sites: Interim Report*, 1998, Technical Report EL-98-, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS). The processes that need to be modeled in the batch systems are transformation reactions and sorption. Advection and dispersion are additional processes that need to be considered in the column systems.

Sorption Equilibrium Modeling. The equilibrium distribution of a solute between the aqueous and solid phases is often assumed to be a linear relationship, particularly at low aqueous-phase solute concentrations. Many systems display nonlinear equilibrium distribution relationships, particularly if aqueous-phase solute concentrations span several orders of magnitude. In this report, a linear model is used to describe sorption equilibrium because it provides an adequate description of the batch equilibrium data provided by WES. A linear model is given by

$$\omega^e = KC^e \tag{1}$$

where the superscript e indicates an equilibrium state, ω is the solid-phase solute concentration, K is a partition coefficient, and C is the aqueous-phase solute concentration.

Sorption Rate Modeling. A popular model for describing sorption rates divides sorption sites into rapidly and slowly sorbing fractions. Equilibrium between the aqueous phase and the solid phase and is given by a combination of linear models

$$\omega^e = \omega^e_f + \omega^e_s \tag{2}$$

$$\omega^e = K_f C^e + K_s C^e \tag{3}$$

where the subscripts f and s indicate rapidly sorbing and slowly sorbing solid-phase fractions, respectively.

A model for describing transformation reactions and mass transfer to rapidly sorbing and slowly sorbing solid phase fractions in a batch reactor is given by

$$\frac{dC}{dt} = -k_a C - \frac{M}{V}\left(\frac{d\omega_f}{dt}\right)_{sorption} - \frac{M}{V}\left(\frac{d\omega_s}{dt}\right)_{sorption} \tag{4}$$

$$\frac{d\omega_f}{dt} = \left(\frac{d\omega_f}{dt}\right)_{sorption} - k_f \omega_f \tag{5}$$

$$\frac{d\omega_s}{dt} = \left(\frac{d\omega_s}{dt}\right)_{sorption} - k_s \omega_s \tag{6}$$

where t is time; k_a, k_f, and k_s are the reaction rate constants for the aqueous phase, the rapidly sorbing solid-phase fraction, and the slowly sorbing solid phase fraction, respectively; M is the solid-phase mass; V is the aqueous-phase volume; and the subscript *sorption* is used to designate an unspecified expression accounting for mass transfer. The rapidly sorbing solid-phase fraction is assumed to always be in equilibrium with the aqueous-phase solute concentration. Under this assumption, substitution of a linear equilibrium model into equation 5 leads to

$$K_f \frac{dC}{dt} = \left(\frac{d\omega_f}{dt}\right)_{sorption} - k_f K_f C \tag{7}$$

Sorption rates for the slowly sorbing fraction are governed by first-order mass transfer, which can be written as

$$\left(\frac{d\omega_s}{dt}\right)_{sorption} = \alpha\left(\omega^e_s - \omega_s\right) \tag{8}$$

where α is a first-order mass transfer coefficient. Substitution of equations 7 and 8 into equation 4, and substitution of equations 8 into equation 6 leads to the coupled equations

$$\left(1+\frac{M}{V}K_f\right)\frac{dC}{dt} = -k_aC - \frac{M}{V}\left(\alpha\left(\omega_s^e - \omega_s\right) + k_fK_fC\right) \tag{9}$$

$$\frac{d\omega_s}{dt} = \alpha\left(\omega_s^e - \omega_s\right) - k_s\omega_s \tag{10}$$

Initial conditions consistent with the modeling approach are

$$C(t = 0) = \frac{M_{solute}}{V + MK_f} \tag{11}$$

$$\omega_s(t = 0) = 0 \tag{12}$$

where M_{solute} is the initial solute mass in the reactor.

An analytical solution can be derived for equations 9 through 12 because linear equilibrium models were used. We developed a computer program that solved these equations numerically to allow for the more general case of nonlinear equilibrium models.

Column Model. Solute transport in the soil column experiments can be adequately modeled as a one-dimensional system with a uniform flow field. The governing system of equations describing fate and transport in the soil column experiments is

$$R_f\frac{\partial C}{\partial t} = D_x\frac{\partial^2 C}{\partial x^2} - v_x\frac{\partial C}{\partial x} - k_aC - \frac{\rho_b}{\theta}\left(\alpha\left(\omega_s^e - \omega_s\right) + k_fK_fC\right) \tag{13}$$

$$\frac{\partial\omega_s}{\partial t} = \alpha\left(\omega_s^e - \omega_s\right) - k_s\omega_s \tag{14}$$

$$R_f = 1 + \frac{\rho_b}{\theta}K_f \tag{15}$$

where R_f is the retardation factor, D_x is the hydrodynamic dispersion coefficient, x is the spatial coordinate, v_x is the mean pore velocity, ρ_b is the bulk density, and θ is the porosity. Boundary and initial conditions for the column reactor are

$$C(x = 0, t) = C_o \tag{16}$$

$$\frac{\partial C(x = L, t)}{\partial t} = 0 \tag{17}$$

4

$$C(0 \le x \le L, t = 0) = 0 \tag{18}$$

$$\omega_s(0 \le x \le L, t = 0) = 0 \tag{19}$$

where C_o is the influent aqueous-phase solute concentration and L is the length of the reactor.

An analytical solution can be derived for equations 13 through 19 because linear equilibrium models were used. However, we solved this problem numerically as a means of demonstrating the iterative split-operator (ISO) algorithm.

Iterative Split-Operator Algorithm. The ISO algorithm is given by: (1) solving the transport portion of the problem over a full time interval, assuming the reaction and mass transfer contributions are known; (2) solving the reaction and mass transfer portion of the problem over a full time interval, assuming the transport contributions are known; and (3) iterating over the first two steps in the algorithm until a convergence criterion is satisfied.

For simplicity in describing the algorithm, we restate equations 13 and 14 in compact operator notation as

$$R_f \frac{\partial C}{\partial t} = L_t + L_{r1} \tag{20}$$

$$\frac{\partial \omega_s}{\partial t} = L_{r2} \tag{21}$$

where

$$L_t = D_x \frac{\partial^2 C}{\partial x^2} - v_x \frac{\partial C}{\partial x} \tag{22}$$

$$L_{r1} = -k_a C - \frac{\rho_b}{\theta} \left(\alpha \left(\omega_s^e - \omega_s \right) + k_f K_f C \right) \tag{23}$$

$$L_{r2} = \alpha \left(\omega_s^e - \omega_s \right) - k_s \omega_s \tag{24}$$

The first step of the algorithm is to obtain a solution over a time step $t \in \{t, t + \Delta t\}$ to an approximation of equation 20. An approximation of equation 20 that decouples it from equation 21 is given by

$$R_f \frac{\partial C}{\partial t} = L_t + \tilde{L}_{r1} \tag{25}$$

where $\widetilde{L}_{r1}$ is an approximation to the reaction operator. If the Crank-Nicolson method is used with a central-difference approximation for L_t, then equation 25 can be rewritten as

$$R_f \frac{C_i^{l+1} - C_i^l}{\Delta t} = \frac{\left(\hat{L}_t\right)_i^{l+1} + \left(\hat{L}_t\right)_i^l}{2} + \left(\widetilde{L}_{r1}\right)_i \quad \text{for } i = 1, n \tag{26}$$

$$\left(\hat{L}_t\right)_i^{l+1} = \frac{D_x}{(\Delta x)^2}\left(C_{i+1}^{l+1} - 2C_i^{l+1} + C_{i-1}^{l+1}\right) - \frac{v_x}{\Delta x}\left(C_{i+1}^{l+1} - C_{i-1}^{l+1}\right) \tag{27}$$

$$\left(\hat{L}_t\right)_i^l = \frac{D_x}{(\Delta x)^2}\left(C_{i+1}^l - 2C_i^l + C_{i-1}^l\right) - \frac{v_x}{\Delta x}\left(C_{i+1}^l - C_{i-1}^l\right) \tag{28}$$

where $\hat{L}_t$ is a central difference approximation for L_t, the subscript i is a nodal index, the superscript l a temporal index, and n is the number of spatial nodes. A reasonable estimate of $\left(\widetilde{L}_{r1}\right)_i$ for the first iteration over the time step $t \in \{t, t + \Delta t\}$ would be the last estimate of $\left(\widetilde{L}_{r1}\right)_i$ from the previous time step $t \in \{t, t - \Delta t\}$. The linear system represented by equation 26 is solved to yield an approximate solution for the $l+1$ time step.

The second step of the algorithm is to obtain a set of solutions over a time step $t \in \{t, t + \Delta t\}$ to an approximation of equations 20 and 21 at each node location. An approximation of these equations that decouples them from the transport portion of the full problem is given by

$$R_f \frac{dC_i}{dt} = \left(\widetilde{L}_t\right)_i + \left(L_{r1}\right)_i \quad \text{for } i = 1, n \tag{29}$$

$$\frac{d\left(\omega_s\right)_i}{dt} = \left(L_{r2}\right)_i \quad \text{for } i = 1, n \tag{30}$$

where $\left(\widetilde{L}_t\right)_i$ is an approximation to the transport operator at node i. $\left(\widetilde{L}_t\right)_i$ can be approximated from the results of the first step of the algorithm as follows

$$\left(\widetilde{L}_t\right)_i = R_f \frac{C_i^{l+1} - C_i^l}{\Delta t} - \left(\widetilde{L}_{r1}\right)_i \quad \text{for } i = 1, n \tag{31}$$

Equations 29 and 30 are solved over a time step $t \in \{t, t + \Delta t\}$ for each node. Methods such as explicit Euler or explicit Runge-Kutta can be used for simple reaction schemes.

More difficult reaction schemes may require routines such as VODE, SODEX, or DASPK. The new estimates of the solution at $t + \Delta t$ are used to calculate a new estimate of the reaction operator $\left(\tilde{L}_{r1}\right)_i$ for the first step of the algorithm. The update is calculated by

$$\left(\tilde{L}_{r1}\right)_i = R_f \frac{C_i^{l+1} - C_i^l}{\Delta t} - \left(\tilde{L}_t\right)_i \quad \text{for } i = 1, n \tag{32}$$

Iteration between the two steps continues until convergence is achieved.

Results

We modeled the sorption and degradation of trinitrotoluene by two soils. The experimental results for the SM silty sand and CL lean clay were used because these soils exhibited the greatest rate-limited sorption of the four soils investigated. Some of the relevant properties of the two soils are given in Table 1.

Table 1. Soil Properties (data provided by WES)				
	% Sand	% Silt	% Clay	% TOC
SM silty sand	85	7.5	7.5	0.020
CL lean clay	65	20	15	0.162

Sorption Equilibrium Experiments. Sorption equilibrium studies were conducted at a solids/liquid ratio of 4 grams to 16 milliliters over a 24 hour period (data provided by WES). Least squares regression was used to fit the linear equilibrium model to the TNT sorption data for the two soils. The results are shown in Figure 1. The partition coefficients for the SM silty sand and CL lean clay are 0.148 and 0.320 cm^3/g, respectively.
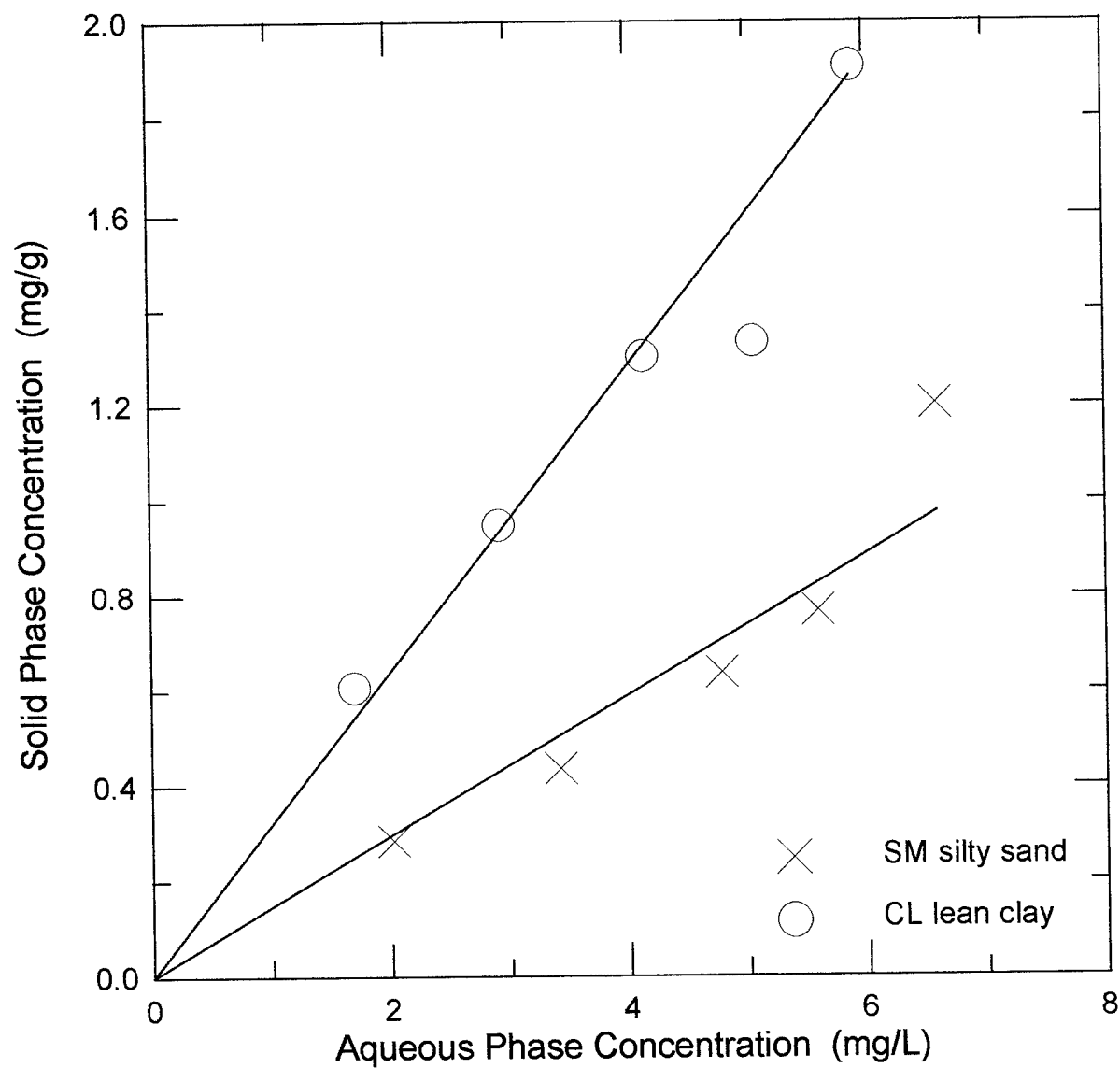
Figure 1. Equilibrium sorption relationships for TNT
on the SM silty sand and CL lean clay.

Sorption Rate Experiments. Sorption rate model parameters can be estimated from the results of sorption rate experiments conducted in batch reactors. The form of the equilibrium relationship needs to be specified. This information is usually derived from the sorption equilibrium experiments. However, there were great discrepancies between the equilibrium observed in the batch equilibrium studies and the batch rate studies. The cause of these discrepancies is unknown. Because of these discrepancies, it became necessary to simultaneously estimate the equilibrium model parameters (i.e., K_f, and K_s) and rate model parameters (i.e., α) from the batch rate experiments. Degradation rate constants were estimated from the column data (discussed later).

Sorption rate studies were conducted at a solids/liquid ratio of 90 grams to 360 milliliters over a 240 hour period (data provided by WES). The results of the batch sorption rate studies and model fits are shown in Figures 2 and 3. There is good agreement between the data and model fits, which is expected given that three parameters were estimated. The model parameters are given in Table 2.

Table 2. Model Parameters from the Batch Rate Experiments					
	K (cm^3/g)	f	K_f (cm^3/g)	K_s (cm^3/g)	α (1/hr)
SM silty sand	1.510	0.484	0.731	0.779	0.0120
CL lean clay	0.606	0.049	0.030	0.576	0.0132

Uptake of TNT by the SM silty sand was greater than uptake by the CL lean clay, which is the opposite of what was observed in the equilibrium studies. The SM silty sand had roughly equal components of fast and slow sorption sites ($f = 0.484$, where $f = K_f / K$). Almost all of the sorption by the CL lean clay was rate limited ($f = 0.049$).
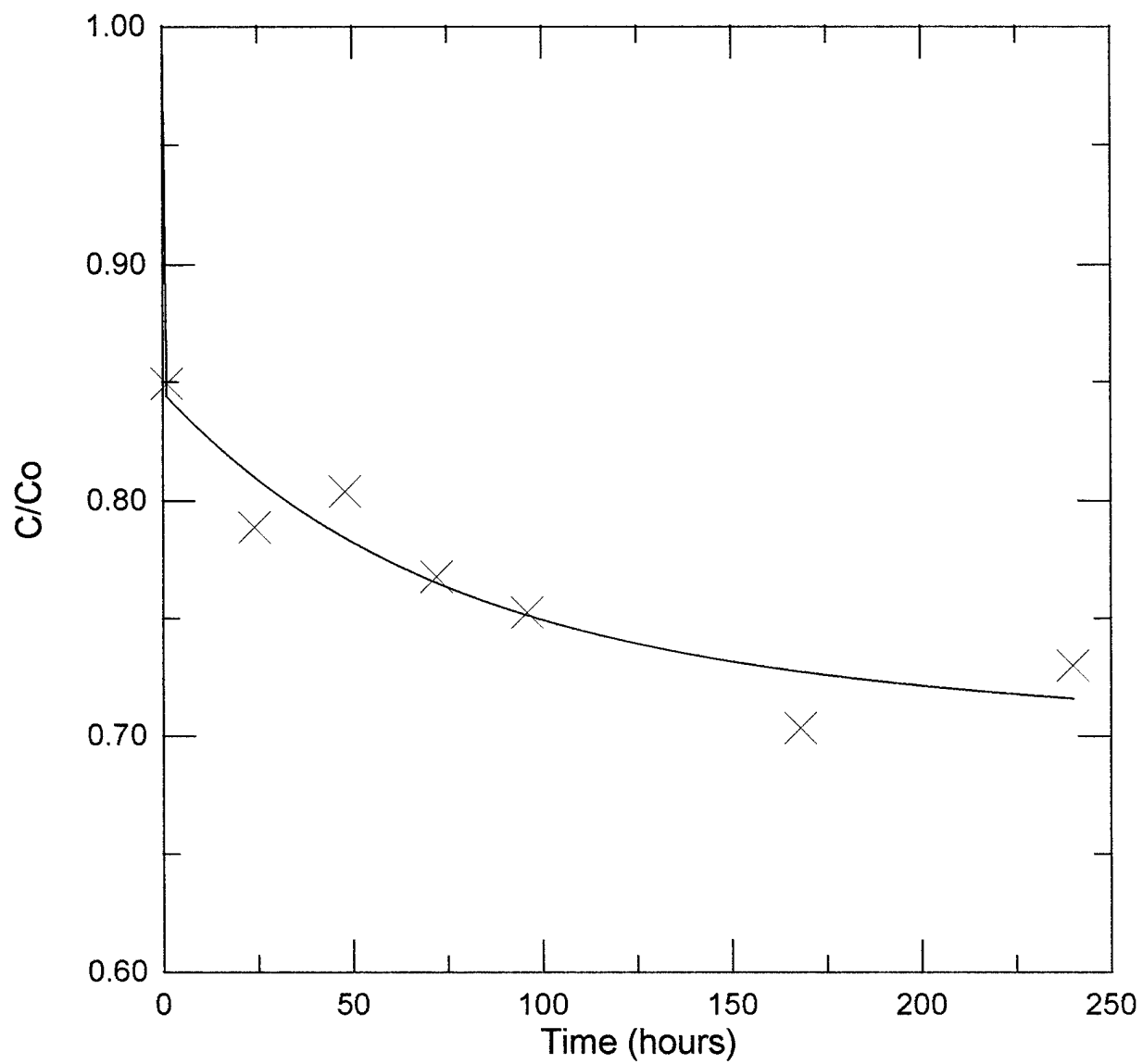
Figure 2. Sorption rate study and model fit for TNT
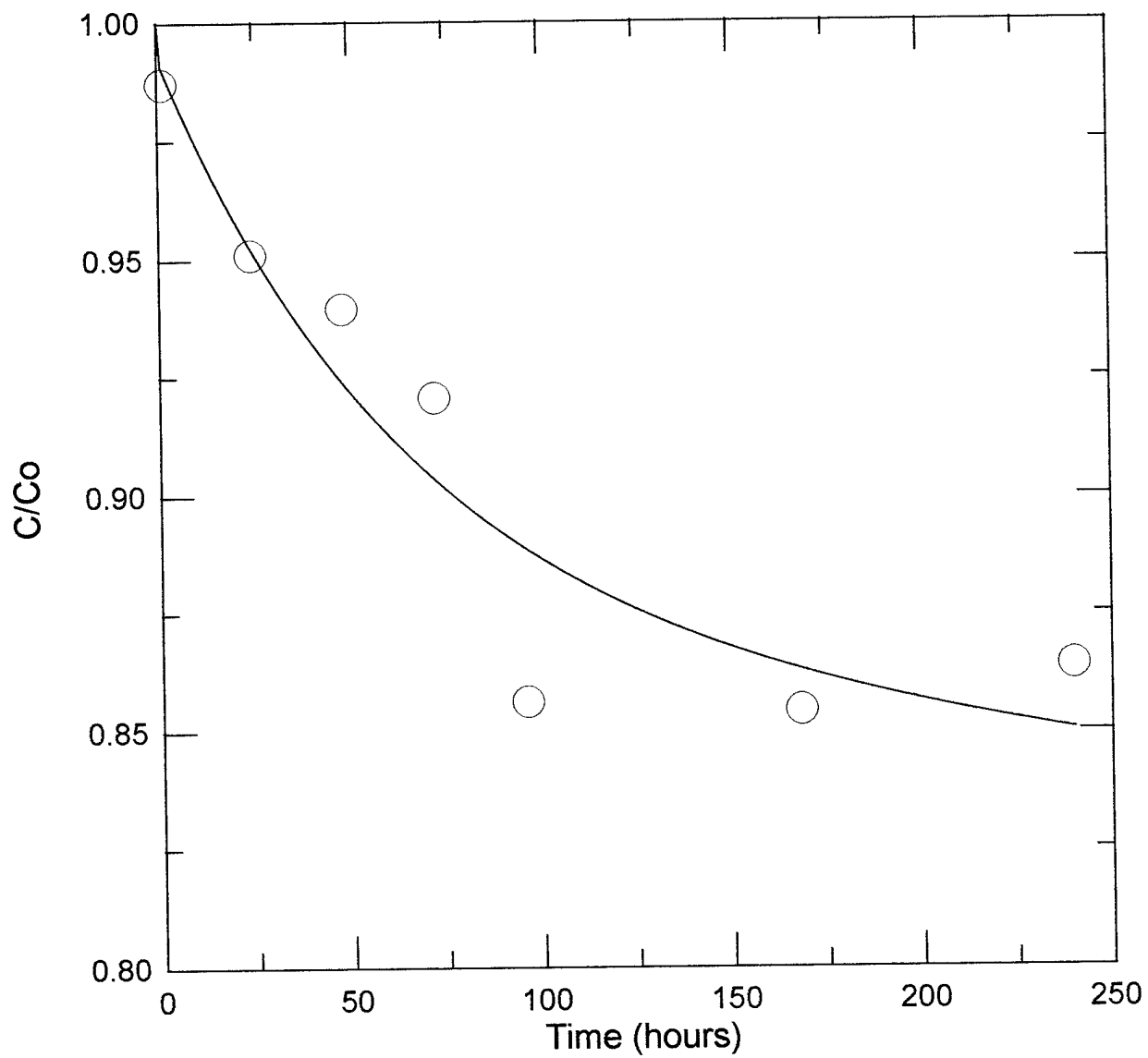on SM silty sand.

Figure 3. Sorption rate study and model fit for TNT
on CL lean clay.

Sorption Column Experiments. The results from two column reactor experiments were modeled. Dispersivity values are needed to accurately model dispersion processes in column experiments. Dispersivity is usually estimated from the results of conservative tracer studies. These studies were not available so a dispersivity of 0.1 cm was assumed. This value is typical for column studies that we have conducted. TNT is known to degrade in these systems so estimates of the reaction rate constants for the aqueous phase, the rapidly sorbing solid-phase fraction, and the slowly sorbing solid phase fraction were needed. We assumed that the three reaction rate constants were the same. The columns achieved steady-state effluent concentrations during the sorption phase of the experiments. The reaction rate constant (k) can be estimated under steady-state conditions by the following equation.

$$k = \frac{-\ln(C_{ss} / C_o)}{\left(1 + \frac{\rho_b}{\theta} K_f + \frac{\rho_b}{\theta} K_s\right) t_h} \tag{33}$$

where C_{ss} is the steady-state effluent concentration and t_h is the hydraulic retention time. Initial attempts to simulate the results from the column experiments using model parameters estimated from the batch experiments were unsuccessful. Therefore, the model parameters (i.e., K_f, K_s, and α) were estimated from the column data. The relevant information and estimated model parameters needed for modeling the column experiments are given in Table 3.

Table 3. Model Parameters from the Column Experiments		
	SM silty sand	CL lean clay
influent concentration (mg/L)	45.85	45.85
pore velocity (cm/hr)	0.389	0.434
dispersion coef. (cm^2/hr)	0.0389	0.0434
bulk density (g/cm^3)	1.14	1.13
porosity	0.459	0.449
decay coef. (1/hr)	8.30×10^{-5}	1.05×10^{-4}
K (cm^3/g)	1.091	0.493
f	0.648	0.570
K_f (cm^3/g)	0.707	0.281
K_s (cm^3/g)	0.384	0.212
α (1/hr)	0.0269	0.172

The experimental and modeling results are shown in Figures 4 and 5. The model results are in good agreement with the data for the sorption phase of both experiments. The model does not accurately simulate the desorption phase of the CL lean clay experiment. The decay coefficients for the SM silty sand and CL lean clay correspond to half lives of 348 and 276 days, respectively. The mass transfer coefficient for the CL lean clay is larger than the mass transfer coefficient for SM silty sand. This is consistent with the lower TNT uptake by the CL lean clay (i.e., the rate of mass transfer is inversely related to sorption uptake).
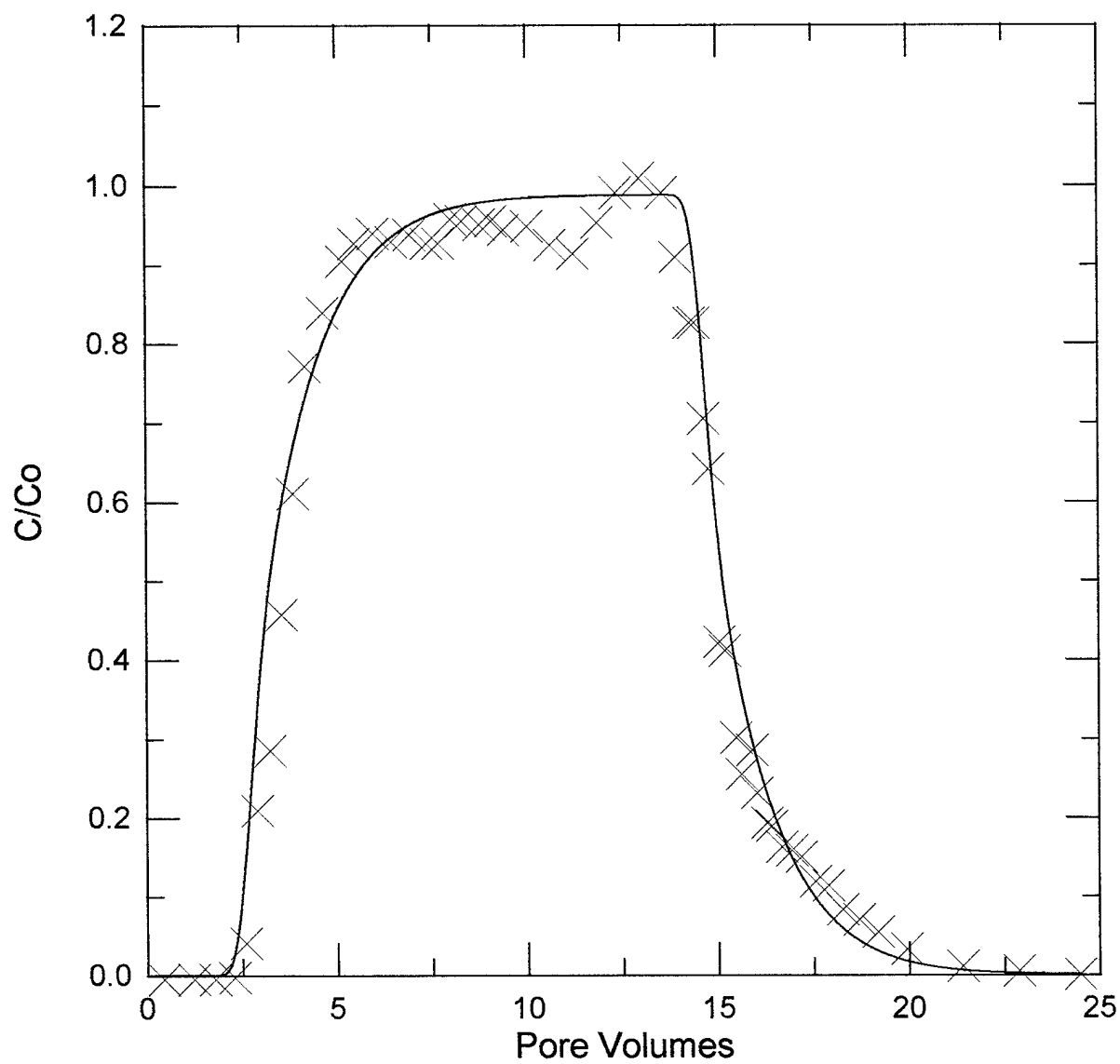
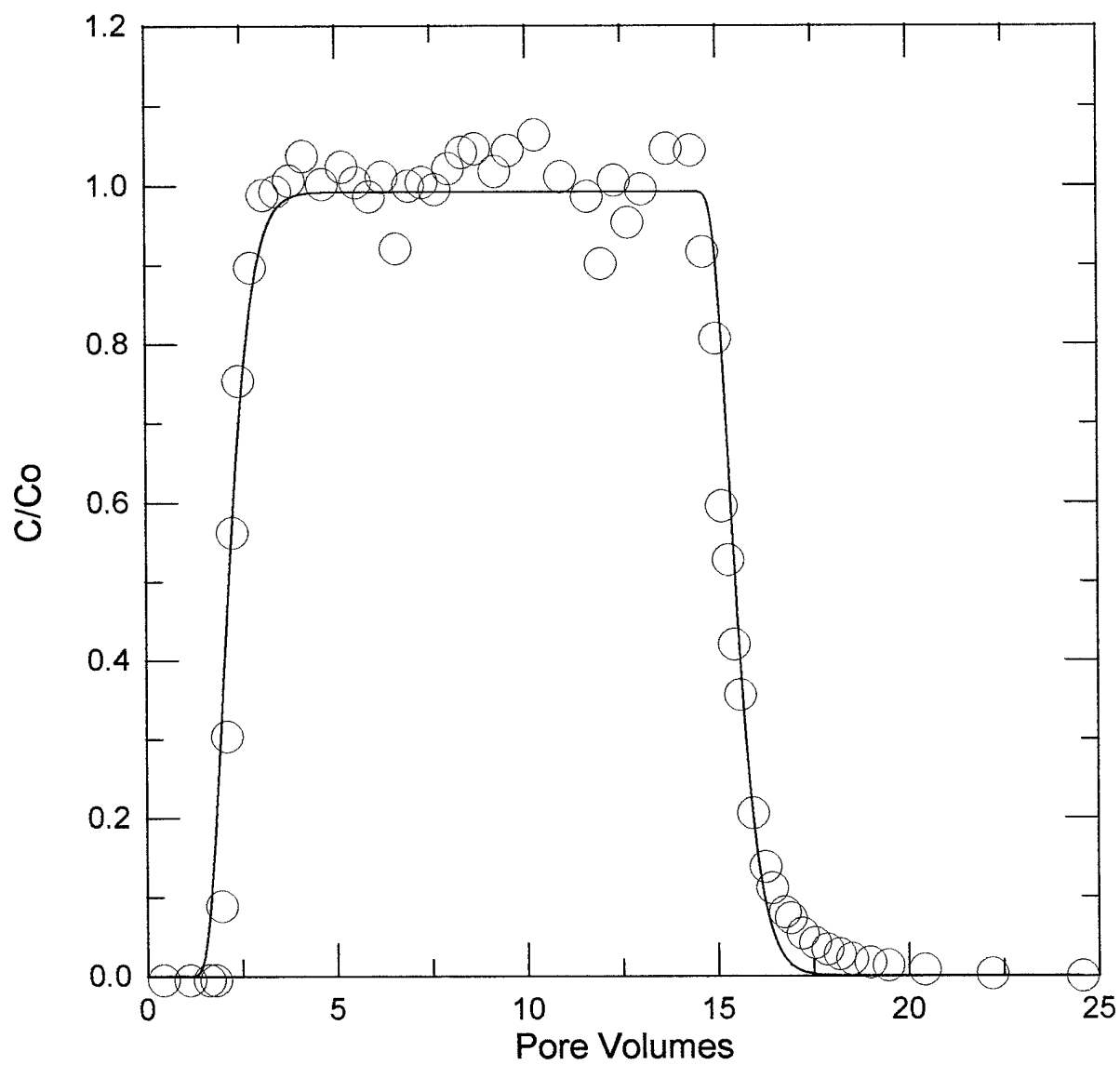Figure 4. Column study and model fit for TNT on SM silty sand.

Figure 5. Column study and model fit for TNT on CL lean clay.